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# Baseline assessment of organic contaminants in surficial sediment from Kachemak Bay, Alaska



Dennis A. Apeti\*, S. Ian Hartwell

National Oceanic and Atmospheric Administration, National Centers for Coastal Ocean Science, United States

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#### ABSTRACT

Organic contaminant inputs to coastal Alaska ecosystems are mostly driven by long range oceanic currents and atmospheric transport from lower latitudes, known as the "grasshopper effect." This study characterized the distribution of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), polychrlorinated biphenyls (PCBs), and a suite of organochlorine pesticides (dichlorodiphenyl tricholoroethane (DDTs), cyclodienes and hexachlorocyclohexanes (HCHs), in five strata in Kachemak Bay, as well as sediment total organic carbon (TOC) content and grain size. PAHs varied broadly throughout the study area. While the presence of substituted naphthalenes might be linked to spilled fuel and oil, incidences of pyrene and alkylated high molecular weight PAHs indicate pyrogenic sources (burned fuel). However, the dominant PAH was perylene (40%–60% of the total PAHs), and is indicative of possible terrestrial weathering (diagenic) input. PCBs, DDTs and the other organochlorine pesticides also varied throughout the study area, but their concentrations along with those of the PAHs were below the National Oceanic and Atmospheric Administration (NOAA) sediment quality guidelines. In most cases, the distributions of the organic contaminants were strongly influenced by the sediment grain size and TOC content, with elevated concentrations being found in depositional areas with fine-grain sediment.

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### 1. Introduction

Sediment contamination in US coastal areas is a major environmental concern because of potential toxic effects on biological resources. Bottom sediments, particularly those that are high in organic matter content, often act as sinks for harmful organic contaminants. The presence of organic contaminants in coastal ecosystems can cause habitat degradation, loss of biodiversity, and coastal food chain contamination, which may ultimately affect human health through the consumption of contaminated fish and wildlife. Thus, characterizing the quality of coastal bottom sediments is important in US particularly in Alaska, which has an extensive coastline of 33,000 miles (greater than the contiguous US), vast natural marine resources, and high subsistence use of marine food sources (US Environmental Protection Agency, EPA 2005).

Located within the Kenai Peninsula in south-central Alaska, Kachemak Bay (Fig. 1) is a nutrient-rich estuarine environment with the Fox and Bradley Rivers in the eastern end of the bay delivering large volumes of freshwater. According to a 2010 ecological assessment by the Kachemak Bay National Estuarine Research

Reserve (KBNERR), the bay sustains diverse marine wildlife of important economic value, such as salmon, Pacific halibut and cod (KBNERR, 2001). The bay supports significant subsistence and recreational fishery resources and is considered one of the most productive bays in the US. However, stocks of diverse commercial fisheries including dungeness crab, cockles, clams have been reported to be declining in recent years (Szarzi et al., 2007; ADF&G, 1998). Studies point to impacts of regime changes including (seas surface temperature, salinity) and anthropogenic activities such as overfishing as the overriding causes of the depressed stocks (Szarzi et al., 2007; North Pacific Fishery Management Council, 2008).

Kachemak Bay was impacted by the Exxon Valdez oil spill (EVOS) of 1989, however the more pressing concern is with the gas industry operations in Cook Inlet. This includes active production platforms, exploration activities (i.e. jack-up rigs), crude-oil transportation via undersea pipelines and on tankers, ballast water treatment, as well as land-based storage tanks with pipelines crossing rivers that lead to Cook Inlet. Discharges associated with oil exploration and production activities include, drilling muds, cuttings, and produced water. Currently there are active federal and state discharge permits allowing the discharge of the aforementioned waste-streams that include hydrocarbons (EPA, 2015, online). However, prevailing ocean currents do not put Kachemak Bay directly "downstream" of these discharges and current sources

<sup>\*</sup> Corresponding author.

E-mail address: dennis.apeti@noaa.gov (D.A. Apeti).

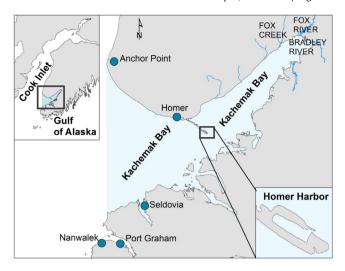


Fig. 1. Map detailing lower Cook Inlet and Kachemak Bay.

of contaminants to the bay are likely more diffuse and many natural occurrences such as volcanic eruptions, natural background source rock, coal, contaminants release from glacial meltwater, and long-range pollutant transport (AMAP, 2005; Ewald et al., 1997; Wania, 1998). There are five active volcanoes on the western side of Cook Inlet. Intermittent eruptions from these volcanoes periodically contribute volcanic ash to the region, including Kachemak Bay, which sits downwind. Snow has been demonstrated to scavenge significant amounts of atmospheric contaminants, which are sequestered in large quantity in glaciers (Grannas et al., 2013). Water-soluble pollutants and compounds that are sorbed onto particulate matter are released in large quantity from snow and glacial meltwaters into the coastal environments (Meyer and Wania, 2008). The 770 km<sup>2</sup> Harding Icefield in the Kenai Peninsula, discharges meltwater into Kachemak Bay. Long-range transport of persistent organic pollutants, by biovectors such as migratory fish (salmon) also by transboundary atmospheric and oceanic currents, are deemed to play an important role in the redistribution and accumulation of persistent contaminants in Alaskan ecosystems (Ewald et al., 1997; Wania, 1998; UNEP, United Nations Environmental Program, 2005). With better understanding in recent years of global geochemical circulation in the Arctic region, there has been increasing concern about the grasshopper effect by which metals and persistent organic pollutants (POPs) from warmer, lower latitudes are being transported and deposited into Alaska's ecosystems (UNEP 2005). Studies have found that arrays of heavy metals and persistent inorganic and organic pollutants (including synthetic organic chemicals and polycyclic aromatic hydrocarbons (PAHs)) from natural sources, industrial, and accidental spills, are finding their way into ecosystems in Alaska (UNEP 2005). Thus, remote Alaskan regions, which were once considered pristine, are now known to be subjected to exposure to contaminants.

Despite its ecological importance and vast natural marine and coastal resources, there are limited baseline data and information to assess future trends in Kachemak Bay. Between 1995 and 1997, the NOAA National Status and Trends Program (NS&T) analyzed contaminants in sediment and mussels collected from a few selected sites in the Gulf of Alaska ( http://egisws02.nos.noaa.gov/nsandt/index.html#; Kimbrough et al., 2008). In collaboration with the US EPA Environmental Monitoring and Assessment Program (EMAP), the Alaska Department of Environmental Conservation, the Alaska Monitoring and Assessment Program (AKMAP) undertook a state-wide coastal ecological condition study that encompassed assessment of contaminants and benthic assemblage in sediment along the western Gulf of Alaska (Saupe et al., 2005).

These studies focused on large region, and while they provide general ideas of regional coastal condition, they lack the monitoring site density and collection frequency necessary to provide enough data for a comprehensive baseline characterization of specific bays like Kachemak Bay.

In collaboration with the Cook Inlet Regional Citizens Advisory Council, and the North Pacific Research Board (NPRB), the NOAA NS&T Program conducted a baseline study to assess the sediment habitat condition in Kachemak Bay. This paper focused on findings of the assessment of organic contaminants in surficial sediment. Using samples collected in 2007 along the northern extent of Kachemak Bay, a suite of organic contaminants including polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and pesticides like butyltins and dichlorodiphenyl trichloroethane (DDT), were measured in the context of evaluating their concentration and spatial distribution in the bay. Additionally, to assess the magnitude of their contamination, concentration levels of organic compounds were compared to published data in the region including the NS&T Program national data base as well as NOAA's sediment quality guidelines for toxicity assessment (Long et al., 1995).

#### 2. Methods

#### 2.1. Study area

Kachemak Bay is a 64 km long glacial fjord on the east side of lower Cook Inlet located in south central Alaska (Fig. 1). An extensive description of the physiography of Kachemak Bay is presented by the Alaska Department of Fish and Game (ADF&G, 1998). The most prominent feature of the bay is Homer Spit, which bisects the Bay into inner and outer portions.

The inner portion of the bay behind the spit is approximately 32 km long. The northern shore has a relatively flat (2.6–11.2 m at high tide) margin that is 1500-2500 m wide. Beyond the margin, the depth falls off to more than 46 m in the middle of the bay. The intertidal zone is characterized by extensive tidal flats below sandy bluffs with numerous coal seams, which may be possible sources of PAHs. The Fox and Bradley Rivers in the eastern end of the bay deliver large volumes of freshwater and glacial till. The south shore has numerous smaller fjords and embayments cut into steep terrain that rises to glaciated valleys and mountain peaks on the Kenai Peninsula. Circulation in Kachemak Bay is driven by a complex interaction between the Alaska Coastal Current, wind and tidal currents, and surface outflow from the inner bay (Burbank, 1977; KBNERR, 2001). The semi-diurnal tidal range in the inner bay is as high as 6 m. The tide and wind fuel the mixing of masses of fresh and saline waters in the inner bay that creates two counterclockwise tidal gyres that tend to deposit sediment in the northern portion of the shelf forming extensive tidal flats (Burbank,

The study area was located on the shelf on the northern half of inner Kachemak Bay, where extensive soft bottom habitats and diverse assemblages of marine organisms are present. A stratified random sampling design was used. This design combines the strengths of a stratified design with the random-probabilistic selection of sampling locations, allowing the data generated within each stratum to be attributed to the dimensions of that stratum with a quantifiable degree of confidence (Heimbuch et al., 1995).

Stratification of the open of the shelf was based on differences in intertidal and subtidal habitats of the shelf as well as the influence of freshwater discharge from the Fox and Bradley Rivers in the east of the bay. As a result, the study area was subdivided into five strata corresponding to different bottom habitats (Fig. 2): Homer Harbor (HH), a distinct semi-enclosed area, was considered a stratum. Homer Harbor, which is periodically dredged, has a different bottom habitat than the open bay. Outside of the harbor,

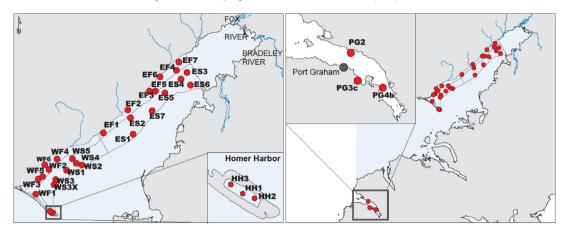


Fig. 2. Maps of Kachemak Bay showing strata and site locations. Left: main study area in inner Kachemak Bay. The insert depicts the Homer Harbor stratum (HH). Right: site location in Port Graham Bay.

the water circulation pattern and the influence of Fox River (Fig. 1) with discharges of silt and sediment create distinct bottom types in eastern and western zones of the bay. Thus, intertidal mudflat and subtidal area of the shelf were each divided into two separate strata, western mudflats (WF) and subtidal zone (WS), the eastern mudflats (EF), and subtidal zone (ES). Using the geospatial modeling environment in ArcGIS®, multiple sampling sites (depending on strata area) were located on a random basis within each stratum. Three sites were located in Homer Harbor; a set of six sites were located in the WS and WF strata, while a set of seven sites were placed in the EF and ES strata (Fig. 2).

Although not part of the original sampling design, three additional random sites were sampled in Port Graham Bay to assess conditions in the vicinity of the Native Alutiiq village of Port Graham, located at the southwest tip of the Kenai Peninsula (Fig. 2). Port Graham Bay is small fjord with the Port Graham River draining into its head to the west. Port Graham Bay is home for abundant natural resources and it supports thriving runs of diverse salmonid species which spawn in the Port Graham River. Sources of pollution in Port Graham Bay may be linked to leaking skeptic tanks, and sewer overflows.

# 2.2. Sampling procedures

Sampling was conducted in 2007 following the NS&T Program's standard field protocols (Apeti et al., 2012). Surficial sediments were collected in triplicate at each site using a Young-modified van Veen grab sampler. From each grab the top 2–3 cm of the sediment was taken and thoroughly mixed into a site composite sample in the field. At each site, clean Kynar coated scoops were used to place the composited sediment into 250 ml pre-labeled Ichem® jars. Extra composited samples were also placed into whirl-Pack bags for grain size analyses. All samples except the grain size analysis samples, were kept frozen at —4 degree until shipped on dryice to the analytical laboratory. Field quality controlled processes included cleaning and rinsing (acetone and then distilled water) all field equipment between sites to reduce possibility of cross contamination.

### 2.3. Chemical analysis

The organic contaminants measured and their respective method detection limits (MDL) are presented in Table 1. Chemical analyses were performed following procedures routinely used by the NOAA NS&T Program (Kimbrough et al., 2007). Aliquots of approximately 1 g of sediment sample were weighed and oven-dried to a constant weight to determine sediment dry-weight. Separate

aliquots of about 30 g of sediment samples were homogenized and chemically dried with Hydromatix<sup>®</sup> and extracted with 100% dichloromethane using the accelerated solvent extraction (ASE) method. The extracts were then concentrated to 3 ml by evaporative solvent reduction. Silica gel/alumina column chromatography was utilized to concentrate and purify the samples before analysis.

Concentration of PAHs and their alkylated homologues were conducted using gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring mode. Chlorinated hydrocarbons (e.g., DDTs, PCBs) were quantitatively determined by capillary gas chromatography with an electron capture detector. Concentrations of butyltins were based on high resolution capillary gas chromatography using flame photometric detection, which quantitatively determined tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT). The concentration of butyltins was expressed in terms of Sn.

Quality control samples were processed in a manner identical to field samples. A method blank was run with every 20 samples, or with every sample batch, whichever was more frequent. Matrix spike/matrix spike duplicate samples were run with every 20 samples, or with every sample batch. The appropriate spiking level was ten times the method detection limit (MDL). National Institute of Standard and Technology (NIST) reference materials were analyzed with each set of samples. Concentration values for all measured organic compounds were reported in ng  $\rm g^{-1}$  dry sediment weight.

Sediment physical parameters such as grain size characterization and total organic carbon content (TOC) were measured following the NS&T methodologies described in McDonald et al. (2006). Sediment grain size was measured using a series of wet sieving and pipetting techniques. Sediment aliquots were first treated with 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) then with deflocculent solution to remove organic matter prior to particle size determination. The treated samples were then poured onto a sieve stack arranged in descending order (i.e., -1 phi and +4 phi), which removed the coarser and sand particles respectively. The remaining solutions with sediment grain <63  $\mu m$  (silt and clay) were allowed to sit undisturbed for 20 s, after which the clay fraction is separated from the silt fraction by pipetting. For the final classification of sediment grain size NS&T program uses the Wentworth scale method with the following major particle size classes: gravel (-2 phi to -5 phi or >4 mm), sand (+4 phi to -1 phi or  $62.5 \mu m - 2$  mm), silt (+5 phi to +7 phi or 4–62.5  $\mu$ m), and clay to colloid (+8 phi and smaller or 1 nm –  $4 \mu m$ ). Total organic carbon was determined using a carbon analyzer. Dried sediment aliquot were treated with phosphoric acid (1:1) to remove inorganic carbon, then combusted at 1350 °C in an oxygen atmosphere. The gaseous phase was then

Table 1

List of organic contaminants analyzed as part of this study.

Butyltins: monobutyltin, dibutyltin, tributyltin, tetrabutyltin

PAHs low molecular weight (2- and 3-ring): Acenaphthene, Acenaphthylene, Anthracene, C1-Benzothiophene, C2-Benzothiophene, C3-Benzothiophene, Biphenyl, Dibenzothiophene, C1-Dibenzothiophenes, C2-Dibenzothiophenes, C3-Dibenzothiophenes, C4-Dibenzothiophenes, C1-Fluorenes, C2-Fluorenes, C3-Dibenzothiophenes, C4-Dibenzothiophenes, C4-Dibenzothiophenes,

C3-Fluorenes, C1-Naphthalenes, C2-Naphthalenes, C3-Naphthalenes, C4-Naphthalenes, Naphthalenes, Phenanthrene, C1-Phenanthrenes, C1-Phenanthrenes, C3-Naphthalenes, C4-Naphthalenes, C4-Naphthalen

C2-Phenanthrenes\_Anthracenes, C3-Phenanthrenes\_Anthracenes, C4-Phenanthrenes\_Anthracenes, **2-methylnaphthalene**; **1-methylnaphthalene**; **2.6-dimethylnaphthalene**, **1,6,7-trimethylnaphthalene**, **1-methylphenanthrenePAHs high molecular weight** (4-ring or more): **Benz[a]anthracene**,

 $\textbf{Benzo[a]pyrene}, \textbf{Benzo[e]pyrene}, \textbf{Benzo[b]fluoranthene}, \textbf{Benzo[g,h,i]perylene}, \textbf{Benzo[k]fluoranthene}, \textbf{Benzothiophene}, \textbf{C1-Chrysenes}, \textbf{C2-Chrysenes}, \textbf{C3-Chrysenes}, \textbf{C3-Chr$ 

C4-Chrysenes, Chrysene, C1-Dibenzo[a,h]anthracene, C2-Dibenzo[a,h]anthracene, C3-Dibenzo[a,h]anthracene, Dibenzonthracene, Fluoranthene,

C1-Fluoranthenes\_Pyrenes, C2-Fluoranthenes\_Pyrenes, C3-Fluoranthenes\_Pyrenes, Indeno[1,2,3-c,d]pyrene, C1-Naphthobenzothiophene,

C3-Naphthobenzothiophene, Naphthobenzothiophene, Perylene, Pyrene, Benzo(ghi)perylene

PCBs: PCB8/5, PCB18, PCB28, PCB29, PCB31, PCB44, PCB45, PCB49, PCB52, PCB56/60, PCB66, PCB70, PCB74/61, PCB87/115, PCB95, PCB99, PCB10/90, PCB105, PCB110/77, PCB118, PCB128, PCB138/160, PCB146, PCB149/123, PCB151, PCB153/132, PCB156/171/202, PCB158, PCB170/190, PCB174, PCB180, PCB183, PCB187, PCB194, PCB195/208, PCB199, PCB201/157/173, PCB206, PCB209

DDTs: ortho and para forms of parent 2, 4'DDT and 4, 4'DDT and metabolites 2, 4'DDE; 4, 4'DDE; 2, 4'DDD; 4, 4'DDD

Cyclodienes: Alpha-Chlordane, Gamma-Chlordane, Oxychlordane, cis-Nonachlor, trans-nonachlor, Heptachlor, Heptachlor-Epoxide, Aldrin, Dieldrin, Endrin

Hexachlorocyclohexanes (HCHs): Alpha-Hexachlorocyclohexane, Beta-Hexachlorocyclohexane, Delta-Hexachlorocyclohexane, Gamma-Hexachlorocyclohexane

Bolded compounds indicate the 24 PAHs and 18 PCBs used for "total" calculations when comparing results from this study to the NOAA Mussel Watch monitoring data in Alaska.

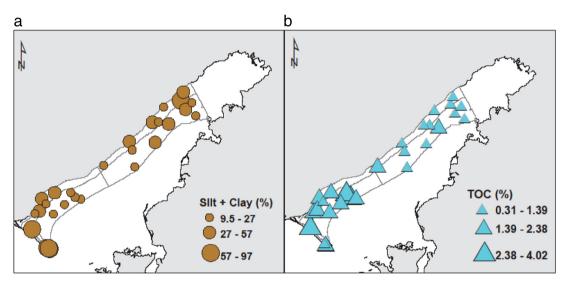


Fig. 3. Spatial distribution of fine sediment (% silt + clay) (a) and total organic carbon (TOC %) (b) in the Kachemak Bay study area.

let to flow through a non-dispersive infrared (NDIR) detection cell to measure CO<sub>2</sub> which is converted to %carbon. Grain size and TOC measurements are reported as percentages of the total sample weight.

### 2.4. Statistical analysis

Primary statistical analyses were conducted using the JMP-5.1<sup>TM</sup> system statistical package. The groups of DDTs, PAHs, PCBs, HCHs, cyclodienes, and butyltins were derived as "total". The "totals" were calculated as arithmetic sum of all the individual congeners or homologues (Table 1). However, in conformity with some published data (NS&T, Mussel Watch data portal, 1997; Saupe et al., 2005), total\_PAH<sub>24</sub> and total\_PCB<sub>18</sub> were also calculated based on 24 PAHs and 18 PCBs highlighted in Table 1.

A normality test using Wilks "goodness of fit" indicated that the data was not normally distributed and as a result, non-parametric statistics were applied. The Wilcoxon Rank Sum test was used for data comparisons. The spatial distributions of organic contaminants, grain size, and TOC, were assessed using multivariate cluster analyses followed by the Wilcoxon test to ascertain the differences between cluster groups. Spearman rank correlation was used to assess the degree of association between TOC and % fine grained sediment, and the concentration of the organic contaminants.

Concentrations of organic contaminants were compared to NOAA NS&T numerical sediment quality guidelines (SQG) developed by Long and Morgan (1990) and Long et al. (1995), known as ERM and ERL (effects range-median, effects range-low). ERL and ERM are statistically derived levels of contamination, above which toxic effects would be expected with at least a 50% frequency (ERM), and below which effects were rarely (<10%) expected (ERL). The mean ERM quotient (Long et al., 1995) is the average of the ratio of the ERM value to sediment concentration for each chemical.

# 3. Results

# 3.1. Sediment grain size and TOC

Fine grain sediment was the sum of the silt + clay fractions. In the study area, sediment grain size composition was fairly broad (Fig. 3). Percent fine grain sediment varied from a low of 9.5% at the ES6 site, to a high of 97% at the HH3 site. At the three sites within Homer Harbor, sediment was finer, with more than 80% fine grained material. Outside the harbor there was no statistical difference between eastern and western strata for sediment grain size content (p > 0.05). However, within the western strata, grain size distribution showed a strong onshore-offshore gradient with sandier materials found at sites closer to shore (p < 0.001), while

**Table 2** Aggregated total concentrations of organic contaminants (ng  $g^{-1}$  dry weight) measured in Kachemak Bay sediments.

Stratum	Station	Latitude	Longitude	Total PAHs	Total PCBs	Total butyltins	Total DDTs	Total cyclodienes	Total HCH
Homer Harbor	HH1	59.6050	-151.4225	1882.4	2.95	9.6	0.47	0.08	0.00
	HH2	59.6044	-151.4208	1689.3	4.64	7.2	0.54	0.46	0.00
	НН3	59.6056	-151.4256	2802.9	3.56	11.4	0.73	0.71	0.00
	EF1	59.6973	-151.2895	261.4	0.44	0.4	0.15	0.08	0.16
	EF2	59.7236	-151.2283	234.3	0.47	0.3	0.01	0.11	0.06
	EF3	59.7446	-151.1739	253.1	0.77	0.5	0.14	0.11	0.06
	EF4	59.7683	-151.1066	84.1	0.31	0.6	0.11	0.20	0.05
	EF5	59.7446	-151.1596	202.2	0.28	0.5	0.16	0.11	0.11
	EF6	59.7614	-151.1466	218.2	0.21	0.6	0.07	0.04	0.06
	EF7	59.7779	-151.0998	213.2	0.14	0.0	0.15	0.12	0.11
	ES1	59.6943	-151.2182	62.5	0.85	0.1	0.06	0.17	0.00
Eastern subtidal	ES2	59.7139	-151.2228	64.7	0.90	0.0	0.10	0.04	0.03
	ES3	59.7651	-151.0811	26.8	0.38	0.1	0.01	0.07	0.05
	ES4	59.7575	-151.0964	58.9	0.60	0.1	0.08	0.06	0.04
	ES5	59.7418	-151.1368	127.2	0.51	0.0	0.14	0.05	0.00
	ES6	59.7499	-151.0740	12.3	0.13	0.0	0.03	0.04	0.00
	ES7	59.7213	-151.1695	154.0	0.66	0.8	0.10	0.00	0.00
Western flat	WF1	59.6275	-151.4586	424.1	0.47	0.3	0.24	0.12	0.07
	WF2	59.6563	-151.4247	199.2	0.27	0.1	0.16	0.06	0.12
	WF3	59.6480	-151.4406	351.3	0.00	0.4	0.27	0.17	0.11
	WF4	59.6684	-151.4040	335.1	0.69	0.7	0.26	0.21	0.16
	WF5	59.6453	-151.4511	333.4	0.58	0.8	0.15	0.01	0.10
	WF6	59.6621	-151.4342	368.9	4.54	0.0	0.15	0.06	0.18
Western subtidal	WS1	59.6545	-151.3824	172.7	0.50	0.0	0.21	0.00	0.00
	WS2	59.6599	-151.3445	168.8	0.98	0.0	0.14	0.06	0.00
	WS3	59.6438	-151.4092	128.8	0.71	0.0	0.16	0.03	0.01
	WS4	59.6623	-151.3579	124.4	0.73	0.0	0.26	0.01	0.00
	WS5	59.6679	-151.3672	156.5	0.66	0.0	0.25	0.0	0.00
Port Graham	PG2	59.3629	-151.8274	249.2	0.67	0.36	0.02	0.22	0.00
	PG3c	59.3449	-151.8196	1264.1	2.86	1.11	0.91	0.15	0.06
	PG4b	59.3397	-151.7876	279.6	1.26	0.0	0.55	0.14	0.00

**Table 3** Spearman rank correlations between organic contaminant distributions and the distribution of fine grained sediment (silt + clay), and TOC content in the sediment (n=29;  $\rho={\rm rho}, p={\rm probability}$ ).

Contaminant	% Fine sedim	ent	% Total organic	% Total organic		
	Spearman	p	Spearman $ ho$	p		
Total PAHs	0.569	< 0.001	0.4715	< 0.001		
Total PCBs	0.137	0.446	0.229	0.200		
Total BTs	0.691	< 0.001	0.204	0.254		
Total DDTs	0.315	0.074	0.619	< 0.001		
Total cyclodienes	0.562	< 0.001	-0.089	0.623		
Total HCHs	0.202	0.259	0.010	0.954		

no real discernable pattern was observed in the eastern strata (Fig. 3).

Total organic carbon ranged from a low of 0.31% to a high of 4.02% (Fig. 3). The distribution of TOC in sediment exhibited a distinct east to west gradient, with Wilcoxon tests indicating a significantly higher TOC content in the western strata compared to the eastern strata (p=0.0001). Like fine grain sediment, the distribution of TOC showed a discernable onshore-offshore gradient in the western strata (Fig. 3), with higher percentages of TOC in the subtidal sites.

# 3.2. Organic contaminant concentrations and distributions

Table 2 illustrates the calculated totals of the contaminant concentrations. The correlation assessments between sediment organic contaminant concentrations and sediment physical characteristics are illustrated in Table 3.

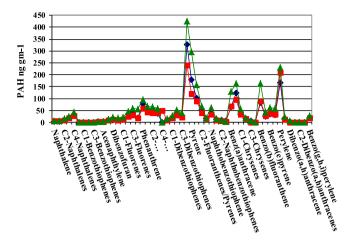
# 3.2.1. PAHs

In sediment samples from Homer Harbor, total PAHs concentration varied from 1700 to over 2800 ng  $g^{-1}$ . Outside of Homer Har-

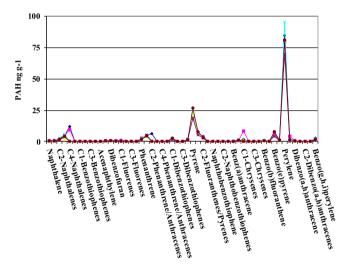
bor, only one location exceeded a concentration of 400 ng  $g^{-1}$  (Table 2). Not only were overall PAH concentrations higher in Homer Harbor than in the rest of Kachemak Bay (p < 0.05), the distributions of individual PAH concentrations in the harbor are distinctly different from those in the bay (Figs. 4 and 5; note the difference in scale). Some small amounts of pyrene are present in the bay, but the dominant PAH in the bay was perylene (40%-60% of the total PAHs). In contrast, elevated concentrations of fluoranthene, pyrene and other unsubstituted high molecular weight compounds, along with lower concentrations of alkylated compounds, were observed in the harbor area. In addition, concentrations of substituted naphthalenes were relatively elevated in the harbor compared to the bay (Figs. 4 and 5). Total PAH concentrations from the three Port Graham Bay sites were also variable. An elevated concentration (1264 ng g<sup>-1</sup>) was recorded in sediment samples collected from PG3c site, which was located in subtidal flats near the village of Port Graham (Table 2). This concentration was however, within the range of total PAH found in sediment from Homer Harbor. At the PG2 site located directly across the bay from the village, and the PG4b site located toward the head of the bay, total PAH concentrations were lower and more comparable to levels found in the open areas of Kachemak Bay (Table 2). NOAA's established SQG for total PAHs are 4022 ng g<sup>-1</sup> and 44 792 ng g<sup>-1</sup> for ERL and ERM, respectively (Long et al. 1995). The PAH concentrations in Homer Harbor are still well below the ERL levels for total PAHs.

# 3.2.2. PCBs

The concentration range of PCBs in Kachemak Bay are illustrated in Table 2. PCBs were detected throughout the study area and their spatial distributions were similar to those of PAHs. Relative to other strata, Homer Harbor had elevated (p = 0.01) PCB concentrations (up to 4 ng g<sup>-1</sup>), while most stations were below 1.0 ng g<sup>-1</sup>. Additionally, elevated (relative to other sites) PCB levels (2.2 ng g<sup>-1</sup>) were detected in the western flat stratum (Table 2).



**Fig. 4.** Concentrations of individual PAHs in sediment from Homer Harbor stations. Results showed good overlaps with no difference among the three Homer Harbor stations.



**Fig. 5.** Concentrations of individual PAHs in subtidal station sediments in the western stratum in Kachemak Bay. Results showed good overlaps with no difference among the stations.

In Port Graham, a concentration of  $2.86~\rm ng~g^{-1}$  was recorded at the PG3c site, but with a mean of  $1.60~\rm ng~g^{-1}$ , total PCB in sediment from Port Graham is equally low and within the range of concentrations in Kachemak Bay. Compared to the NOAA's SQGs for total PCBs ( $22.7~\rm ng~g^{-1}$  for ERL and  $180~\rm ng~g^{-1}$  for ERM), PCB concentrations in the study area were very low; even concentrations in Homer Harbor were well below the ERM and ERL values. As illustrated in Table 3, PCB concentrations across the study area were not significantly correlated with the sediment physical parameters of grain size (p=0.446) or TOC content (p=0.200).

#### 3.2.3. Butyltins

Butyltins were detected mostly in Homer Harbor and in Port Graham (Table 2). In Homer Harbor, concentrations of total butyltins ranged from 7.2 to over 11 ng g $^{-1}$ , with the mean value higher than that of other strata (p=0.0001). Based on data from all the sites, Spearman Rank correlation coefficients indicated that butyltin concentrations in sediment were strongly correlated (p<0.001) with sediment grain size (Table 3).

# 3.2.4. DDTs and other pesticides

Organochlorine pesticides were detected throughout the study area (Table 2). Total DDTs concentration was significantly correlated with sediment TOC, but not grain size (Table 3). DDTs and

other pesticides were also detected at all three Port Graham sites (Table 2). Concentrations of these organic compounds in sediment samples from Port Graham were generally comparable to those found in the main study area of Kachemak Bay. Unlike the other pesticides, SQG have been defined for total DDTs as  $1.58 \text{ ng g}^{-1}$  for ERL, and 46.1 ng  $g^{-1}$  for ERM (Long et al., 1995). Total DDTs concentrations in sediment from Kachemak Bay were well below the NOAA's SOG ERL value. Cyclodiene insecticides (chlordanes, heptachlors, nonachlors, aldrin, dieldrin, endrin) were also found at most sites in the study area, but concentrations were very low. Hexachlorocyclohexanes (HCHs), which include alpha, beta, delta and gamma (lindane), were not detected in the Homer Harbor stratum, but were found above detection limits, and more frequently, in the intertidal mudflat areas (Table 2). Consequently, their distribution was poorly correlated (P < 0.05) with grain size and TOC in the sediment. Overall, the concentrations of the organochlorine pesticides in Kachemak Bay were very low.

## 4. Discussion

It is important to recognize that the Homer stations are the only locations in the data set that are specifically located in an active harbor. All the other sites are away from harbor activity and reflect ambient background conditions. Relative to regional sediment data from the 1995-1997 Mussel Watch stations (NS&T data portal http://egisws02.nos.noaa.gov/nsandt/index.html#), concentrations of PAHs in Kachemak Bay were relatively higher than the others, with the exception of the east Nahku Bay site near Skagway in the northern panhandle (Table 4). The explanation for the PAH concentrations in the fjord where Skagway is located is not as straight forward, and may be related to water circulation patterns. The station near Skagway is at the head of a highly constricted system where flushing may not be efficient. However, the rest of the PAH values in Kachemak Bay in the present study were comparable to those found by the environmental monitoring and assessment project (EMAP) assessment in south-central Alaska, which reported values ranging from a low of 1.66 ng g<sup>-1</sup> to a high of 840 ng  $g^{-1}$  for total PAHs (Saupe et al., 2005). This indicates that the concentration range for total PAHs found in Kachemak Bay proper were generally within the regional averages.

PAH signatures include both petrogenic and pyrogenic sources. Petrogenic PAHs can originate from natural releases from petroleum and coal deposits, or from anthropogenic sources such as non-point sources runoff, permitted discharges or spills. Pyrogenic PAHs are formed primarily as a result of fossil fuel combustion and forest fires, but also during volcanic eruption (ATSDR, 1995). The relative proportion of low and high molecular weight PAHs, and the distribution of parent PAHs versus their alkyl homologues, have been used as indicators to discern sources and weathering of PAH contamination (Zeng and Vista, 1997; Baumard et al., 1998). High proportions of low molecular weight PAHs are typically associated with oil and petroleum releases (petrogenic source). A high proportion of high weight PAHs is often linked to combustion byproducts and/or long-term weathering. The elevated concentrations of pyrene and other unsubstituted high molecular weight compounds, with lower concentrations of alkylated compounds in the harbor and open bay (Figs. 4 and 5), are indicative of pyrogenic sources. The concentrations of substituted naphthalenes in the harbor are elevated relative to the bay as well, which further indicate the contribution of spilled fuel and oil. Outside the harbor, the largest component of PAHs was, by far, perylene (Fig. 5). This is a natural by-product of the breakdown of terrestrial plant material (National Research Council, 1985). Thus, inside Homer Harbor, and to some extent at Port Graham, the sediment has a typical signature of oil and fuel spills, as well as exhaust from boat engines. While the results indicate the contribution of anthropogenic PAHs

Table 4

Organic contaminant concentrations (ng g<sup>-1</sup>) from the present study (mean ± sdt E) compared to average Mussel Watch (MW) data from southern Alaska (Cook Inlet Homer Spit (CIHS), Port Valdez Mineral Creek (PVMC), Nahku Bay east Skagway, and PWS = average of 5 sites in Prince William Sound), and EMAP (Saupe et al., 2005).

Element	This study		1997 Mussel Watch monitoring data				EMAP Alaska	
	Homer Harbor	Open bay	CIHS1997	PVMC	Skagway	PWS	EMAP (Saupe et al., 2005)	
PAHs	$2073 \pm 33.6$	$181 \pm 22$	90.1	10.2	4607	47.3	$224\pm194$	
PAH/without pyrene	$1860 \pm 323$	$87 \pm 12$	59.3	10	4552	46	nd	
PCBs	$3.69 \pm 0.5$	$0.65 \pm 0.2$	2.3	0.52	23.75	0.52	nd	
Butyltins	$9.4 \pm 1.2$	$0.27 \pm 0.06$	0.0	0.0	0.0	0.0	nd	
DDTS	$0.57 \pm 0.1$	$0.14 \pm 0.02$	0.61	0.87	1.39	0.11	nd	
Cyclodiene	$0.6 \pm 0.2$	$0.21 \pm 0.02$	1.22	0.13	5.27	0.11	nd	
HCHs	0	$0.03 \pm 0.01$	0.39	0.38	0.84	0.1	nd	

Total PAHs and PCBs were based on the 24 PAHs and 18 PCBs highlighted in Table 1. nd denotes no-detect. Total PAHs for the EMAP Alaska study was based on 21 PAHs not including pyrene although pyrene was detected.

is extremely limited, the presence of numerous coal seams in the geologic formations around Kachemak Bay might constitute possible natural sources.

Whether from natural or anthropogenic sources, PAHs can be toxic in the environment. A number of PAHs, including benzo[a] pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, and indeno[1, 2, 3-c, d]pyrene have been linked to carcinogenicity in vertebrates (USDHHS, 1995). Although fish metabolize PAHs, Hylland (2006) found that exposure to PAHs can cause oxidative stress, immune and endocrine system dysfunction, as well as developmental abnormalities in fish. Hose et al. (1982) demonstrated that exposure to a concentration of 0.1 µg benzo[a]pyrene for five days resulted in reduced and delayed hatch in the eggs of the sand sole Psettichthys melanostictus. However, while PAHs were considerably elevated in Homer Harbor compared to concentrations found in the open bay, levels were still well below the ERL guidelines for total PAHs, suggesting that the concentration of PAHs alone is unlikely to cause sediment toxicity across the study area.

Butyltins are a class of organometallic compounds used as biocides in antifouling paints (Birchenough et al., 2002; Bennett, 1996). Since 1989, the use of tributyltin (TBT) as an antifouling agent was banned in the US on non-aluminum vessels smaller than 25 m in length (Gibbs and Bryan, 1996). In the environment, the parent compound, tri-butyltin, can be degraded and transformed to form the metabolites dibutyltin, monobutyltin, as well as inorganic tin. However, depending on environmental conditions, tri-butyltin can last for years in bottom sediments (Batley, 1996). Because of its widespread use, tri-butyltin and its metabolites continue to be detected in all components of the environment. Butyltins were mainly observed in Homer Harbor, and when compared to other locations in Alaska, butyltin concentrations in Homer Harbor were extremely elevated (Table 4). The presence of butyltins in Kachemak Bay, especially in the harbor area, is likely linked to the previous use of antifouling paint applied to boat hulls. The sloughing paint chips from hulls, and the slow release from the paint into the water and uncontrolled runoff from power washing hulls that fell directly into the harbor, increased ambient environmental concentrations that persist to this day. Butyltins, particularly tri-butyltin, are linked to endocrine disruption, specifically imposex (females developing male characteristics) in marine gastropods and other mollusks (e.g., mussels), as well as abnormal shell development and poor weight gain (Batley, 1996; Strand et al., 2009). In sea otters from Alaska, Murata et al. (2008) found linkages between butyltin concentration and immunotoxicity and hepatotoxicity. Also, Frouin et al. (2008) reported that butyltins, and di-butyltin in particular, could pose a serious threat to the immune functions in harbor seals.

PCBs are synthetic compounds that have been used in numerous applications, ranging from electrical transformers and capacitors, to hydraulic and heat transfer fluids, to pesticide and paints.

Although no longer manufactured in the US, ecosystem contamination by PCBs is widespread due to their environmental persistence and tendency to bioaccumulate (IPCS, 1993). It has been shown that PCBs can cause a variety of serious health effects, including immune, hormonal, reproductive, and nervous systems damage in wildlife (EPA, 2008). Exposure to PCBs in fish has been linked to reduced growth and reproductive impairment (EPA, 2008).

Organochlorine pesticides are typically neurotoxins, but DDTs have also been shown to interfere with the endocrine system (ATSDR, 2002a). DDT, and its metabolite DDE, for example, were specifically linked to eggshell thinning in apex predatory birds. A number of organochlorine pesticides are also toxic to aquatic life, including crayfish, shrimp and fish (ATSDR, 2005; WHO, 2006). Because of their persistence and heavy use in the past, residues of many organochlorine pesticides can be found in the environment, where they continue to be of environmental concern (Butler, 1973). Because of their adverse health effects, particularly to wildlife, the use of DDTs and other pesticides were banned in the US in 1970s (ATSDR, 2002b). Along with butyltins, PCBs and all measured synthetic organochlorine pesticides are persistent organic pollutants (POPs). The cyclodienes and DDTs have accumulated in the fine grained, organically enriched sediments in Homer Harbor. Their concentrations in the open bay are very low. The HCH concentrations do not follow that pattern, however, but tend to accumulate in the intertidal sediments, as opposed to the harbor or other subtidal areas. Although the concentrations of these organochlorine pesticides were low relative to SQG values, their detection in Kachemak Bay speaks to their widespread environmental persistence.

Although these anthropogenic POPs were not produced, or perhaps heavily used in Alaska, the presence of compounds such as PCBs, DDTs, HCHs and cyclodiene insecticides above detection limits in Kachemak Bay suggests long range atmospheric transport. A number of reports by the Arctic Monitoring Assessment Program (AMAP) have seemingly identified the so called grasshopper effect as the major contributors to ecosystem contamination in Alaska (AMAP, 2009). Thus, POPs, such as chlorinated pesticides (e.g. DDTs) and industrial contaminants (e.g. polychlorinated biphenyls or PCBs) emitted as a result of anthropogenic activities in the Americas, Europe, and Asia, could be transported and deposited in Alaska's coastal areas.

### 5. Conclusion

Residues of PAHs, PCBs, butyltins, and pesticides were detected throughout the Kachemak Bay study area. Elevated levels of pyrogenic and petrogenic PAHs were observed in the harbor, but concentrations were below toxic levels and there was no evidence of residual oil from past major spills. In most cases, the concentrations of organic contaminants were strongly influenced by the sediment grain size and TOC. Concentrations in Homer Harbor were elevated relative to the rest of strata, however, levels were below the

NOAA sediment quality guidelines. There are no reliable records of pesticide use in south central Alaska, and with no known industrial point sources in the region, the presence of organic contaminants above detection limits in a relatively remote and sparsely populated area like Kachemak Bay highlight their environmental persistence and the possible contribution of long range atmospheric and oceanic circulation patterns. The results of this study serve as baseline data for unforeseen events and future reference for sediment contamination in Kachemak Bay.

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